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Synthesis, physical characterization, and biological activity of some Schiff base derive from substituted aniline and it's complexes with (Co, Ni) transition metal ion's

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ABSTRACT

Transition metal (Co , Ni) as acetate salt , complexes of Salicylaldehyde derived Schiff base were synthesized and characterized by CHN analysis and FTIR spectra , the synthesized Schiff base ligand was in (1:2) molar ratio toward metal ion's using spectrophotometric , all the complexes were evaluated for their thermal degradation studies using TG analytical method in static air , thermodynamic parameters were calculated from the TG curve (ΔS , ΔH , ΔG) the ligand and it's metal complexes were expected to show an interesting bioactivity

Key words: Schiff base , FTIR-spectra , thermodynamic parameters

INTRODUCTION

HugoSchiff describes the condensation between an aldehyde and an amine leading to a **Schiff base** in 1864[1] , metal ion's through imine nitrogen and other groups usually linked to the aldehyde [2], N,S and O donor atoms show broad biological activity and are special interest due to of the variety of way in which they are bonded metal ion's[3] , Schiff base derived from aromatic amines and aromatic aldehyde have a wide variety of application in many field biological , inorganic and analytical chemistry [4,5], because of their ability to act as didentate ligands for transition metal ion's [6], they have recently received considerable attention due tois good performanticin coordination chemistry [7], unique antibacterial , anticancer and other physical activities [8], in this work we wish to report synthesis and characterization a thermodynamic behaviors of such class of new ligands having (C=N) and (OH) groups toward its probable color , reaction and stabilities with (Co , Ni) metal ion's using spectrophotometric analysis in different temperature .

MATERIALS AND METHODS

2-1. material: all chemicals and solvents used wereof analytical reagent grad purchased from fluka and BDH , metal(II)(Co , Ni) as acetate partially dehydrated of salts were carried out by drying in oven for several hours at 100-110C°

2-2. Instrumental: Element analysis (CHN) was carried out by Perkin Elmer 2400 series IICHN Elemental Analyzer, FTIR spectra were recorded using Shimadzu,FTIR-8400S-JAPAN, melting point were recorded on VeeGODijital model VMP-D (Jenway), UV-Visible spectra were record on U.V-9200BIOTECHENGINEERING MANAGEMENT CO.LTD (UK)Single beam.

2-3. synthesis:

2-3-1. synthesis of salicylidene-2-bromo-4-methyl aniline: (0.372 gm/ 2mmol)of 2-bromo-4-methyl aniline dissolve in warm 10 ml ethanoland mixed with equivalent amount of warm corresponding salicylaldehyde (0.244 gm / 2mmol) in warm 10 ml ethanol , added two drops of glacial acetic acid , the mixture was left reflex for 2h , then solid product formed , was separated by filtration and purified by recrystallization from ethanol , washed with ethanol and then dried .

2-3-2. synthesis of salicylidene-4-methoxy aniline: (0.246/ 2 mmol)of 4-methoxy aniline dissolve in warm 10 ml ethanoland mixed with equivalent amount of warm corresponding salicylaldehyde (0.244 gm / 2mmol) in warm 10 ml ethanol , added two drops of glacial acetic acid , the mixture was left reflex for 2h , then solid product formed , was separated by filtration and purified by recrystallization from ethanol , washed with ethanol and then dried .

2-4. preparation of Schiff base transition metal complex:

An ethanolic solution of (0.29 gm / 1 mmol) of salisyldene-2-bromo-4 methyl aniline was added to ethanolic solution of (0.088 gm / 0.5 mmol) of $Ni(AC)_2$ mixture was stirred , reflexed for 2h , the solid product was obtain , filtered , washed with ethanol then dried

$$CH_3C_6H_4BrNH_2+OHC_6H_4CHO\rightarrow C_{14}H_{12}ONBr$$

$$2C_{14}H_{12}ONBr+Ni(AC)_2\rightarrow Ni(C_{14}H_{11}ONBr)_2+2ACH$$

An ethanolic solution of (0.29 gm / 1 mmol) of salisyldene-2-bromo-4 methyl aniline was added to ethanolic solution of (0.088 gm / 0.5 mmol) of $Co(AC)_2$ mixture was stirred , reflexed for 2h , the solid product was obtain , filtered , washed with ethanol then dried

$$CH_3C_6H_4BrNH_2+OHC_6H_4CHO\rightarrow C_{14}H_{12}ONBr$$

$$2C_{14}H_{12}ONBr+Co(AC)_2\rightarrow Co(C_{14}H_{11}ONBr)_2+2ACH$$

An ethanolic solution of(0..227 gm /1 mmol) of salisyldene-4-methoxy aniline was added to ethanolic solution of (0.088 gm / 0.5 mmol) of $Ni(AC)_2$ mixture was stirred , reflexed for 2h , the solid product was obtain , filtered , washed with ethanol then dried

$$OCH_3C_6H_4NH_2+OHC_6H_4CHO\rightarrow C_{14}H_{13}O_2N$$

$$2C_{14}H_{13}O_2N+Ni(AC)_2\rightarrow Ni(C_{14}H_{12}O_2N)_2+2ACH$$

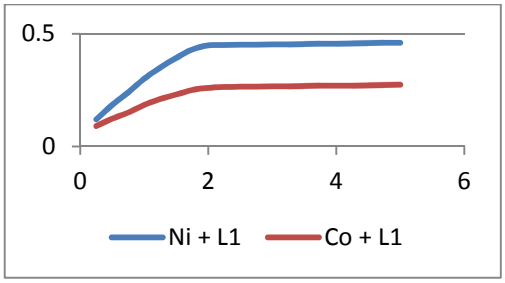
An ethanolic solution of(0..227 gm /1 mmol) of salisyldene-4-methoxy aniline was added to ethanolic solution of (0.088 gm / 0.5 mmol) of $Co(AC)_2$ mixture was stirred , reflexed for 2h , the solid product was obtain , filtered , washed with ethanol then dried

$$OCH_3C_6H_4NH_2+OHC_6H_4CHO\rightarrow C_{14}H_{13}O_2N$$

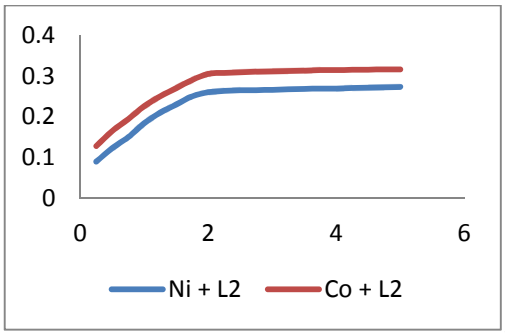
$$2C_{14}H_{13}O_2N+Co(AC)_2\rightarrow Co(C_{14}H_{12}O_2N)_2+2ACH$$

RESULTS AND DISCUSSION

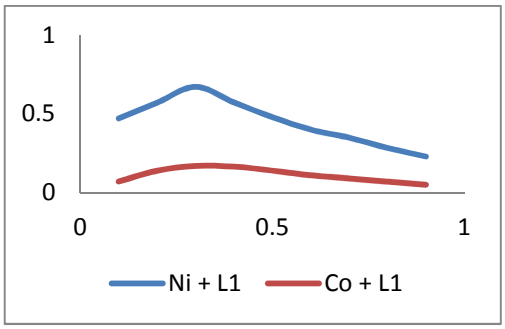
3-1. In order to obtain a clue about the stiochemistry and stability of ligand complex with (Co , Ni) ion's preliminary studies were performed for investigation of the ligand complexation with metal ion's in ethanolic solution[9], spectrophotometerically , using the concentration of ligand (1×10^{-4} M)in ethanolic solution was kept of constant , and the UV-Visible spectra of the result solution at various M^{+2} / L mole ratio and continuous variation were recorded until desired mole ratio[10], was reached the absorption spectra indicating the formation of stable (1:2) (M/L) complexinethanolic solution .as it obvious from fig below



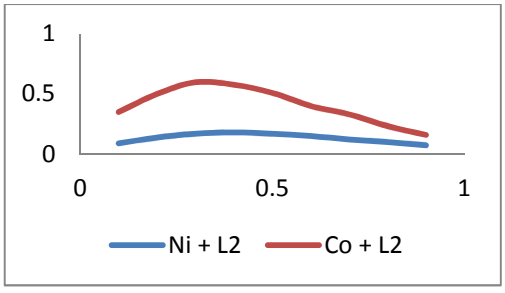
Fig(1):UV-Visible spectra by mole ratio method



Fig(2):UV-Visible spectra by mole ratio method



Fig(3):UV-Visible spectra by continuous variationmethod



Fig(4):UV-Visible spectra by continuous variation method

3-2. All the physical measurement of the synthesized ligand , the metal complexes and the expected formula of synthesized complexes are shown in table (1)the data are very near to the expected formula to all the prepared compound[11]

3-3.The FTIR-spectra and the metal complexes:

spectra of ligand tables(3 and 4) showabsence of band at 1735cm^{-1} (C=O) due to the carbonyl and 3473 cm^{-1} due to NH_2stretching vibration and a strong new band appeared at 1630 cm^{-1} assigned to azomethene (HC=N) which indicate that amine and aldehyde of starting material are absent and have been converted into the new bonding (azomethene bond)

Table (1) physical properties of the synthesized compound

compound	color	Yield %	m.p	Kstability	%founded (calculated)			
					%C	%H	%N	%res.
L_1	yellow	90.1	69	-	57.91 (57.93)	4.29 (4.14)	4.84 (4.93)	32.96 (33)
$Co(L_1)_2$	dim gray	75.5	275	2.3×10^8	52.5 (52.75)	3.6 (3.45)	4.44 (4.39)	39.46 (39.41)
$Ni(L_1)_2$	dark green	83.7	>300	3.1×10^8	52.6 (52.75)	3.32 (3.45)	4.5 (4.39)	39.58 (39.41)
L_2	green	93.3	93	-	74.01 (74.00)	5.858 (5.73)	6.20 (6.17)	13.932 (14.1)
$Co(L_2)_2$	maroon	77	280	1.6×10^8	65.6 (65.75)	4.75 (4.70)	5.5 (5.48)	24.15 (24.07)
$Ni(L_2)_2$	green yellow	80.6	190	1.2×10^8	65.62 (65.75)	4.65 (4.70)	5.45 (5.48)	24.28 (24.07)

Note: $L_1 = C_{14}H_{12}ONBr$, $L_2 = C_{14}H_{13}O_2N$

Table (2) the most significant IR band of ligand and it metal complexes in cm^{-1}

compound	NH_2	C-H alphatic	C=N	C=O	C=C	C-H aromatic
S	-	-	-	1735	1575	3130
N1	3473&3381	2850	-	-	1590	3059
L_1	-	2830	1616	-	1610	3188
N2	3421&3344	-	-	-	1580	3005
L_2	-	-	1630	-	1600	3053

Note: $L_1 = C_{14}H_{12}ONBr$, $L_2 = C_{14}H_{13}O_2N$, $N1=C_7H_8NBr$, $N2=C_7H_9NO$, S=Salicylaldehyde

3-4.TG analysis:

Thermal degradation of Schiff base ligand and their corresponding metal complexes which we studied in rang of 40-800 C°, Table (5) shown the temperature at which maximum loss of species under study occurred at this temperature is called (T_s) temperature at the maximum stop[12].

Table (3) thermodynamic parameters of metal complexes

compound	T_s	ΔG	ΔH	ΔS	stages
$Co(L_1)_2$	677	8932	65146	72.7	2
$Ni(L_1)_2$	678	10282	15069	6.2	1
$Co(L_2)_2$	678	19280	19953	0.9	2
$Ni(L_2)_2$	530	18573	13605	-6.4	2

Note: $L_1 = C_{14}H_{12}ONBr$, $L_2 = C_{14}H_{13}O_2N$

The thermal degradradation of $Co(L_1)_2$:

$$Co(C_{14}H_{12}ONBr)_2+O2\rightarrow 2CO+H_2O+N_2+CoC_{26}H_{22}OBr_2$$

$$CoC_{26}H_{22}OBr_2+O_2\rightarrow Br_2+CoO+2CO_2+2C_{12}H_{11}O$$

The thermal degradradation of $Ni(L_1)_2$:

$$Ni(C_{14}H_{12}ONBr)_2+O_2\rightarrow 2CO_2+N_2+Br_2+C_{26}H_{24}CoO$$

The thermal degradradation of $Co(L_2)_2$:

$$Co(C_{14}H_{13}O_2N)_2+O_2\rightarrow N_2+2H_2O+C_{28}H_{22}CoO$$

$$C_{28}H_{22}CoO+O_2\rightarrow 2CO+2CO_2+C_{24}H_{22}CoO$$

The thermal degradradation of $Ni(L_2)_2$:

$$Ni(C_{14}H_{13}O_2N)_2+O_2\rightarrow 2CO_2+N_2+C_{26}H_{26}NiO$$

$$C_{26}H_{26}NiO+O_2\rightarrow 2H_2O+2CO_2+C_{24}H_{22}NiO$$

3-5. Biological activity :

The reactivity of synthetic protects toward the biological systems is an important feature of the current research and Schiff base of transition metal complexes play significant role in this direction , the result of antibacterial are given below

Table (4) antibacterial activity data for the ligand and it's metal complexes

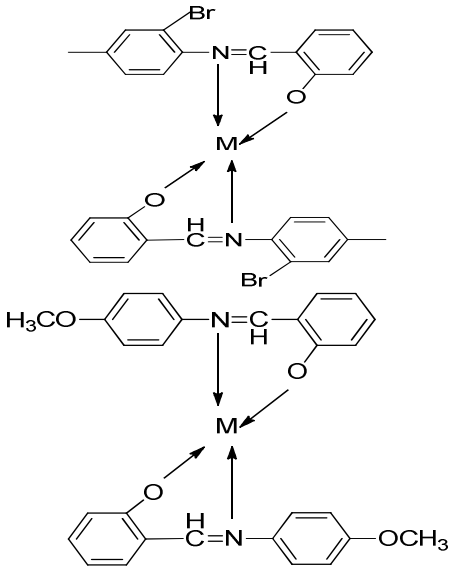
compound	*Aeromomashydrophila*(-)	*Staphylococcus aureus* (+)
L_1	-	10
$Co(L_1)_2$	-	12
$Ni(L_1)_2$	-	-
L_2	-	10
$Co(L_2)_2$	-	-
$Ni(L_2)_2$	-	10

Note: L1 = C14H12ONBr , L2 = C14H13O2N

CONCLUSION

In this paper we report the synthesis full spectroscopic characterization of Schiff base which was coupled with (Co and Ni) as dehydrated acetate salt to form stable complexes , the stability of these metal ions complex record at different temperature to calculate the thermodynamic parameters (ΔS,ΔH,ΔG) both ligand and complex were characterized based on FTIRand physic-chemically analysis , on the biological assays both are found to be active on bacterial activity , further analysis such as elemental analysis study is to be carried out to confirm the structure of ligand and its complexes.

3-6. the expected structure of the metal complexes are shown in figure (1)



M = Co and Ni

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